Short Communications

Investigation of the Disproportionation of the α-Tocopheryl Radical on the Basis of Dipole Approximation

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Essentially three effects contribute to the interaction of molecules if one disregards the chemical bond: They are

a) dispersion forces caused by mutually induced electric moments,
b) inductive effects, *i.e.* induced electric multipole moments caused by incompletely shielded nuclear charges or by permanent dipole moments, and
c) orientation effects arising through dipole-dipole interactions between the electric molecular moments or bond moments.

In an atom the electron density decreases exponentially with increasing distance from the nucleus *i.e.* the chemical bond is not a long range effect in the quantum mechanical sense of overlapping of electron densities of two atoms. However, dispersion forces and induction effects become operative over longer distances, both of them decreasing with the sixth power of the atomic distance, while dipole-dipole interactions, on the other hand, decrease only with the third power of the distance. For molecules with permanent electric dipole moments or with bond moments, inner rotations, orientation in a liquid lattice and librations can be explained and calculated through dipole-dipole interactions.[1]

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In this investigation, from the different possible disproportionation steps of the tocopheryl radical the energetically most favoured mutual orientation is selected on
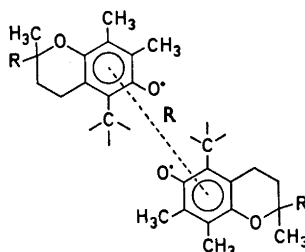
5 - 6 - Disproportionation
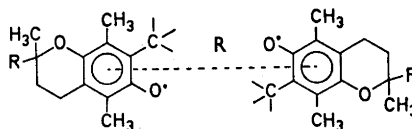
6 - 7 - Disproportionation

Fig. 1. Two models of disproportionation of the α-tocopheryl radical.

the basis of dipole-dipole interactions. One may infer from this to the most reactive position of the molecule. It is essential to note in this respect that the electron density obtained from semi-empiric quantum mechanical calculations does not favour any position of the molecule in this special example, as far as reactivity is concerned.[1] Developing charge distributions in molecules to electric multipole moments has been used to calculate quadrupole moments.[3] If the total charge of a molecule is equal to zero, the Taylor series for the
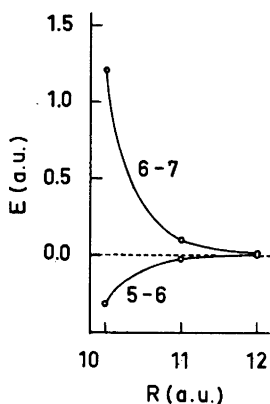
Fig. 2. Dipole-dipole interaction energies over distance R.

development of the charge distribution starts with a term containing the dipole moment of the charge distribution. The bond dipole moments may be obtained from quantum mechanical calculations if they are not measurable.[4]

As an example the hindered inner rotation of ethane may be considered. Setting the bond moments $\vec{p_i}$ at the center of the C—H bond one can compute their interaction energies by

$$E_{12} = (\vec{p_1}\vec{p_2} - 3\vec{r_{12}}\vec{p_1} \cdot \vec{r_{12}}\vec{p_2}/r_{12}{}^2)/|r_{12}|^3$$

with $\vec{r_{12}}$ being the vector from the first to the second dipole moment. For the energy barrier of 1.2 kcal/mole about 50 % of the measured value is obtained. The position of the two hydroxyl groups of catechol was measured. For this example, calculation yields correct values for the bond energy of the hydrogen bridge.

In the α-tocopheryl radical the most favoured position of the methyl groups was selected by estimating the minimum dipole-dipole interactions out of one thousand positions of rotation. Next, the energy diagrams for two α-tocopheryl radicals were calculated; in the first model positions 5 and 6 are approaching one another, in the second case positions 6 and 7 (Fig. 1). Fig. 2 shows the corresponding energy diagrams. The interaction energies may not quantitatively be correct for smaller distances. The most important result, however, is the different shape of the two diagrams. An

approach of positions 6 and 7 results in a repulsion curve, while in an approach of positions 5 and 6 the energy decreases, thus allowing for disproportionation.

These results support the following experimental evidence: monovalent oxidation of α-tocopherol proceeds *via* the α-tocopheryl radical (phenoxy radical) to the intermediary *ortho*-quinone methide,[5,6] finally yielding a single spirodienone ether.[5] The favoured reactivity of position 5 which results in the formation of ether bonds at this position in all examples has been observed by Nilsson *et al.*[6] for the tocols and chromanols. Computation of the dipole-dipole interactions of these model compounds in a fashion analogous to α-tocopherol confirms these results.

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Note on the Pigments of Some *Drosera* Species

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7-Methyljuglone (5-hydroxy-7-methyl-1, 4-naphthoquinone) and plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) seem to be fairly common constituents of many *Drosera* species although their co-occurrence has previously only been proved in two of seventeen investigated species.[1] We now report their co-occurrence in three more species. As earlier reported[2] both *Drosera intermedia* and *D. anglica* contain plumbagin, 3-chloroplumbagin, 2-methyl-naphthazarin (5,8-dihydroxy-2-methyl-1,4-